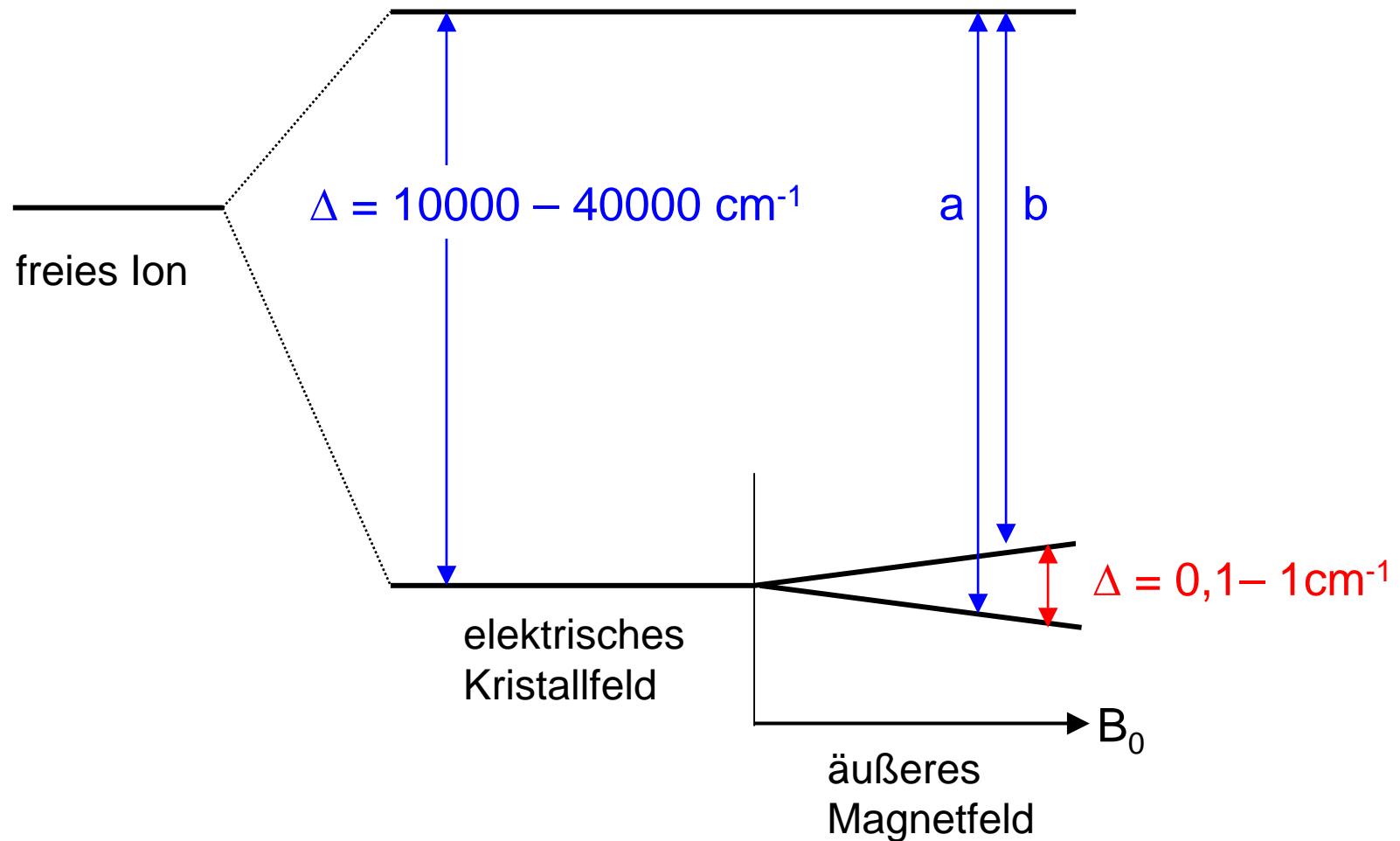


# Einfluss eines äußeren Magnetfeldes

---

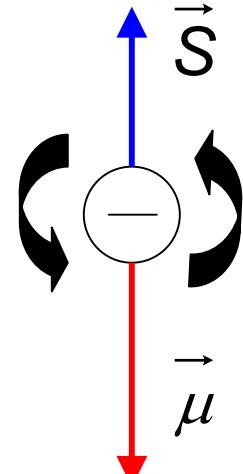


# Spin und magnetisches Moment von Elektronen und Kernen

---

**Elektron**

$$|\vec{S}| = \hbar \sqrt{S(S+1)}$$



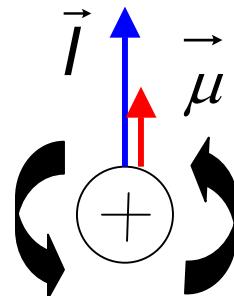
$$\vec{\mu}_e = -g_e \beta \vec{S}$$

$$\beta = e\hbar / 4\pi mc$$

$$|\vec{\mu}_e| = 658 |\vec{\mu}_p|$$

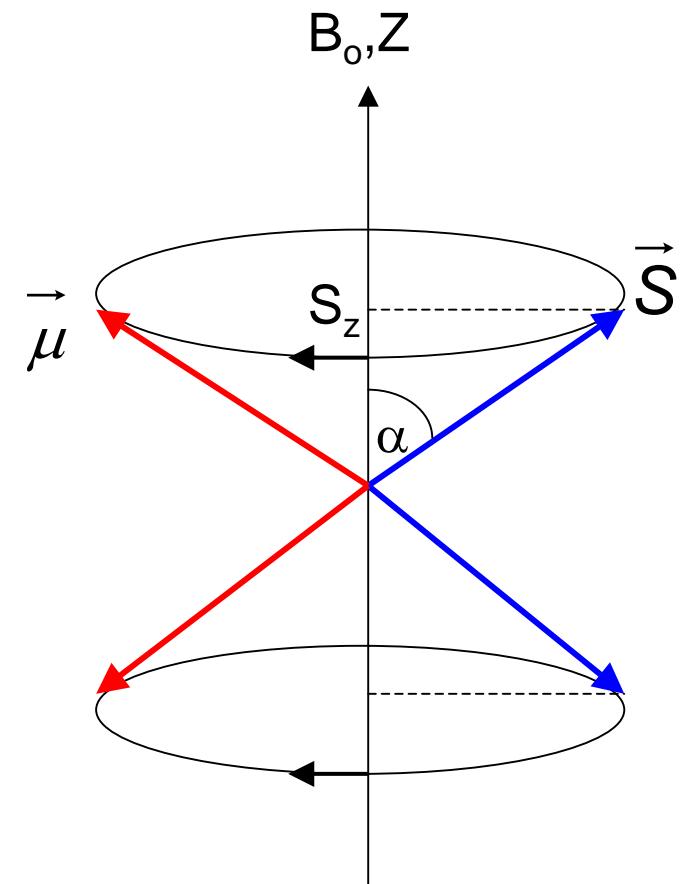
**Proton**

$$|\vec{I}| = \hbar \sqrt{I(I+1)}$$



$$\vec{\mu}_p = -g_n \beta_n \vec{I}$$

**Elektron im Magnetfeld**



$$S_z = \cos \alpha |\vec{S}| = \pm 1/2$$

# Information accessible by EPR

- local structure of transition metal ions with unpaired electrons:

d <sup>1</sup>	d <sup>2</sup>	d <sup>3</sup>	d <sup>4</sup>	d <sup>5</sup>	d <sup>6</sup>	d <sup>7</sup>	d <sup>8</sup>	d <sup>9</sup>
V <sup>4+</sup>	V <sup>3+</sup>	Mn <sup>4+</sup>	Mn <sup>3+</sup>	Mn <sup>2+</sup>		Ni <sup>3+</sup>	Ni <sup>2+</sup>	Ni <sup>+</sup>
Mo <sup>5+</sup>	Mo <sup>4+</sup>	Mo <sup>3+</sup>		Fe <sup>3+</sup>	Fe <sup>2+</sup>	Rh <sup>2+</sup>	Rh <sup>+</sup>	Rh <sup>0</sup>
Cr <sup>5+</sup>		Cr <sup>3+</sup>	Cr <sup>2+</sup>	Ru <sup>3+</sup>	Ru <sup>2+</sup>		Pt <sup>2+</sup>	Pt <sup>+</sup>
Ti <sup>3+</sup>				Os <sup>3+</sup>	Os <sup>2+</sup>	Pd <sup>3+</sup>	Pd <sup>2+</sup>	Pd <sup>+</sup>
Zr <sup>3+</sup>				Ir <sup>4+</sup>	Co <sup>3+</sup>	Co <sup>2+</sup>	Co <sup>+</sup>	
							Ag <sup>2+</sup>	
							Au <sup>2+</sup>	
							Cu <sup>2+</sup>	

## Information accessible by EPR

---

- local structure of transition metal ions with unpaired electrons:

d <sup>1</sup>		d <sup>3</sup>		d <sup>5</sup>		d <sup>7</sup>		d <sup>9</sup>
V <sup>4+</sup>		Mn <sup>4+</sup>		Mn <sup>2+</sup>		Ni <sup>3+</sup>		Ni <sup>+</sup>
Mo <sup>5+</sup>		Mo <sup>3+</sup>		Fe <sup>3+</sup>		Rh <sup>2+</sup>		Rh <sup>0</sup>
Cr <sup>5+</sup>		Cr <sup>3+</sup>		Ru <sup>3+</sup>		Pd <sup>3+</sup>		Pt <sup>+</sup>
Ti <sup>3+</sup>				Os <sup>3+</sup>		Co <sup>2+</sup>		Pd <sup>+</sup>
Zr <sup>3+</sup>				Ir <sup>4+</sup>				Ag <sup>2+</sup>
		visible at elevated T						
								Au <sup>2+</sup>
								Cu <sup>2+</sup>

- nature of radicals ( $\bullet\text{C}_x\text{H}_y$ ,  $\bullet\text{O}_2^-$ ,  $\bullet\text{O}^-$ ,  $\bullet\text{OH}$ ,  $\bullet\text{OOH}$ )
- conduction electrons of small metal particles
- size and shape of ferro- or ferrimagnetic resonance of metal particles (e. g. Ni<sup>0</sup>) or metal oxide particles (e. g. Fe<sub>3</sub>O<sub>4</sub>)

# Energie von Elektronen im äußeren Magnetfeld

---

$$E = -\vec{\mu} \cdot \vec{B}$$

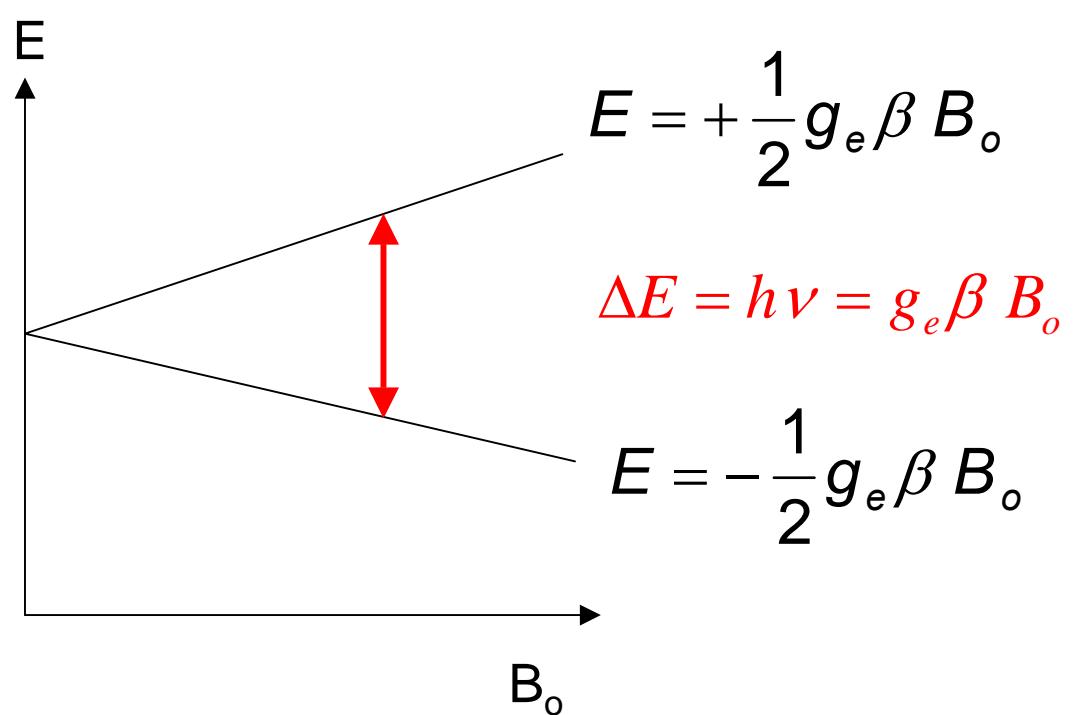
$$H\Psi = E\Psi$$

$$H = g_e \beta \vec{S} \cdot \vec{B}$$

$$H = g_e \beta S_z B_o$$

$$E = g_e \beta m_s B_o$$

## Freies Elektron

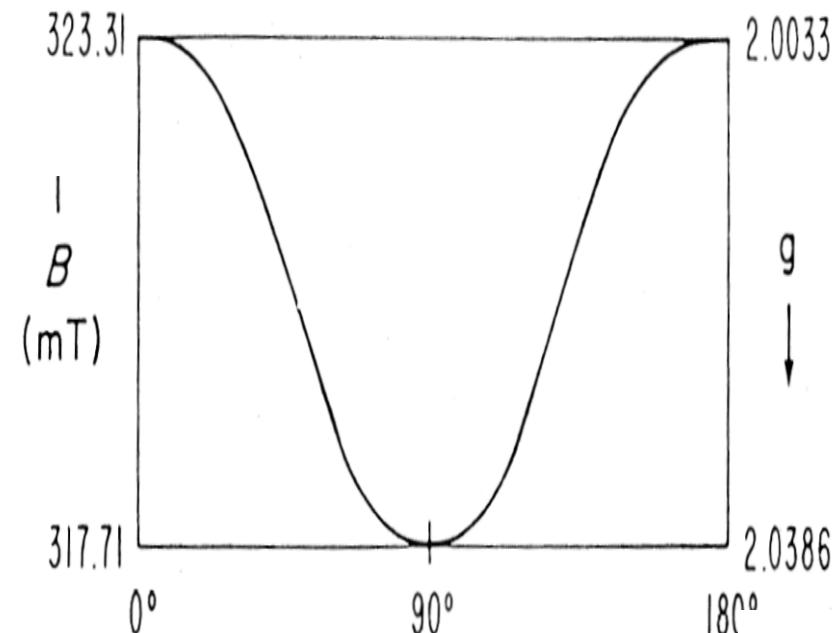
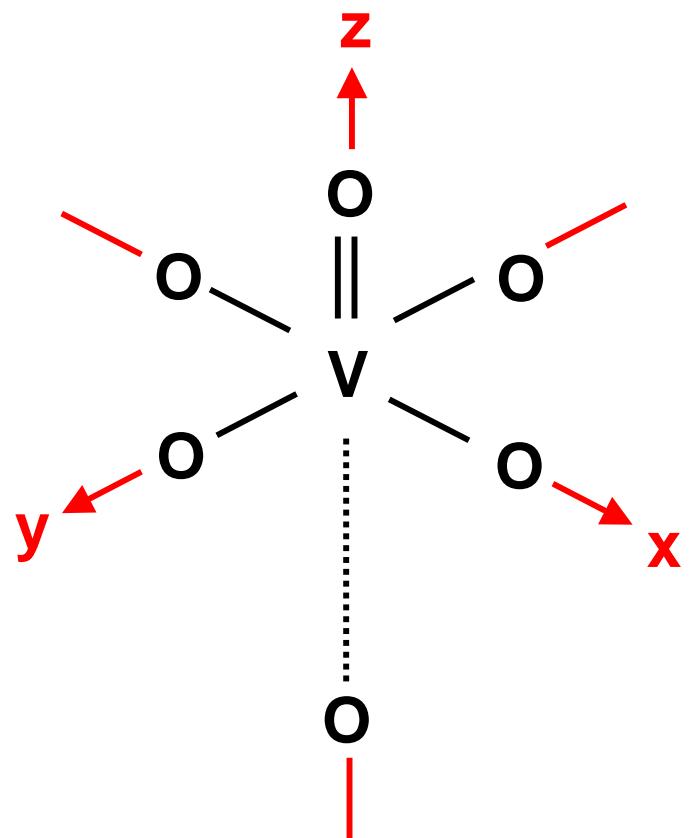


## Elektron in einem Atom

$$H = \beta \vec{B} \cdot (\vec{L} + g_e \vec{S}) + \lambda \vec{L} \cdot \vec{S} = \beta \vec{B} \cdot g \cdot \vec{S}$$

## g - Anisotropie des ESR-Spektrums von VO<sup>2+</sup>

---



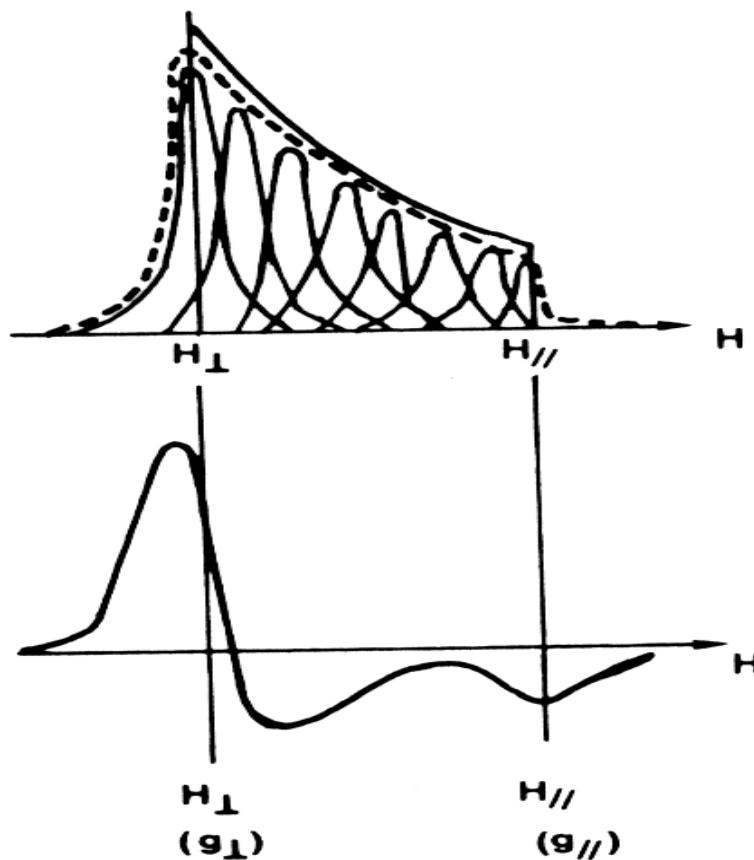
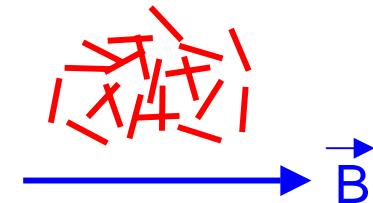
$$g_{\text{eff}}^2 = g_{\parallel}^2 \cos^2 \Theta + g_{\perp}^2 \sin^2 \Theta$$

$$H = \beta [g_{\perp}(B_x \hat{S}_x + B_y \hat{S}_y) + g_{\parallel} B_z \hat{S}_z] = \beta \vec{B} \cdot \hat{g} \cdot \hat{S}$$

# Pulver-ESR-Spektrum

---

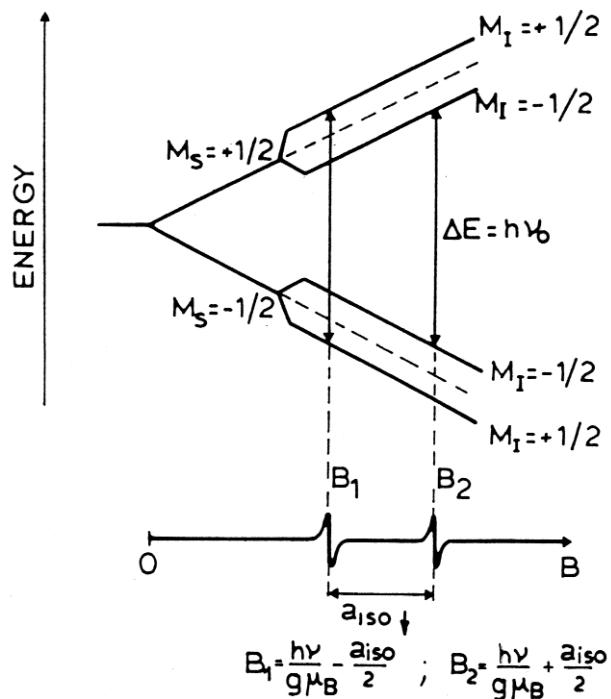
Summe über alle möglichen Orientierungen der magnetischen Achsen von  $\text{VO}^{2+}$  gegenüber  $\vec{B}$



# Kopplung von Elektronen- und Kernspin

---

$$S = \frac{1}{2}, I = \frac{1}{2}$$



**Beispiel:**

H-Atom

$$a_{iso} = 50,68 \text{ mT}$$

Anzahl der Hyperfeinlinien:

$$(2I_1 + 1) (2I_2 + 1) \dots (2I_n + 1)$$

Bei Kopplung mit  $n$  äquivalenten Kernen:

$$(2nl + 1)$$

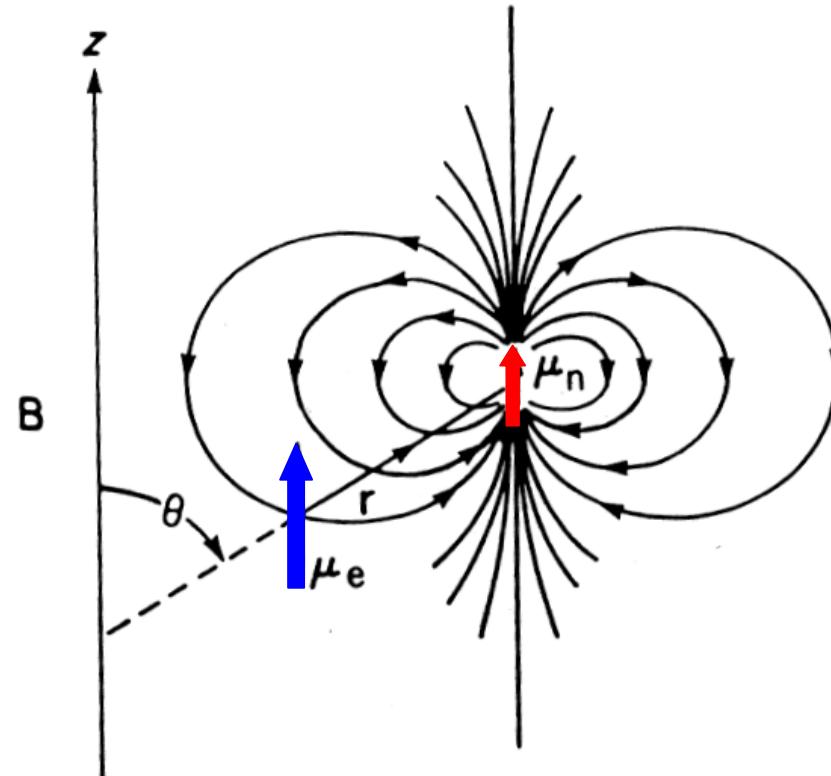
$$A_{iso} = \frac{2\mu_0}{3} g \beta_e g_n \beta_n |\psi(0)|^2$$

# Anisotropie der Hyperfeinkopplung von VO<sup>2+</sup>

---

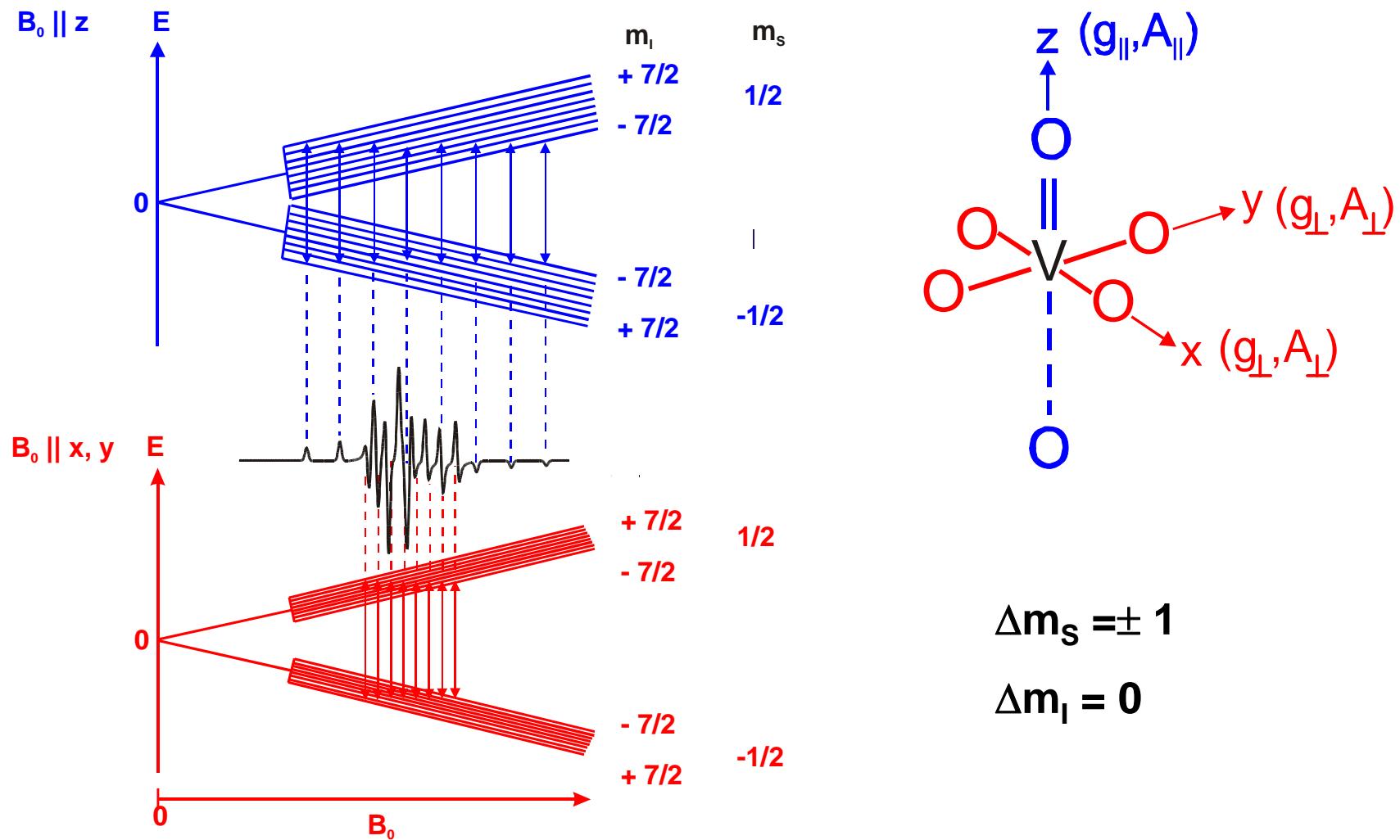
Kopplung von  $\vec{S}$  und  $\vec{I}$   
für V:  $I = 7/2$

Aufspaltung jedes  
Elektronenniveaus in  
 $(2I + 1) = 8$   
Hyperfeinniveaus

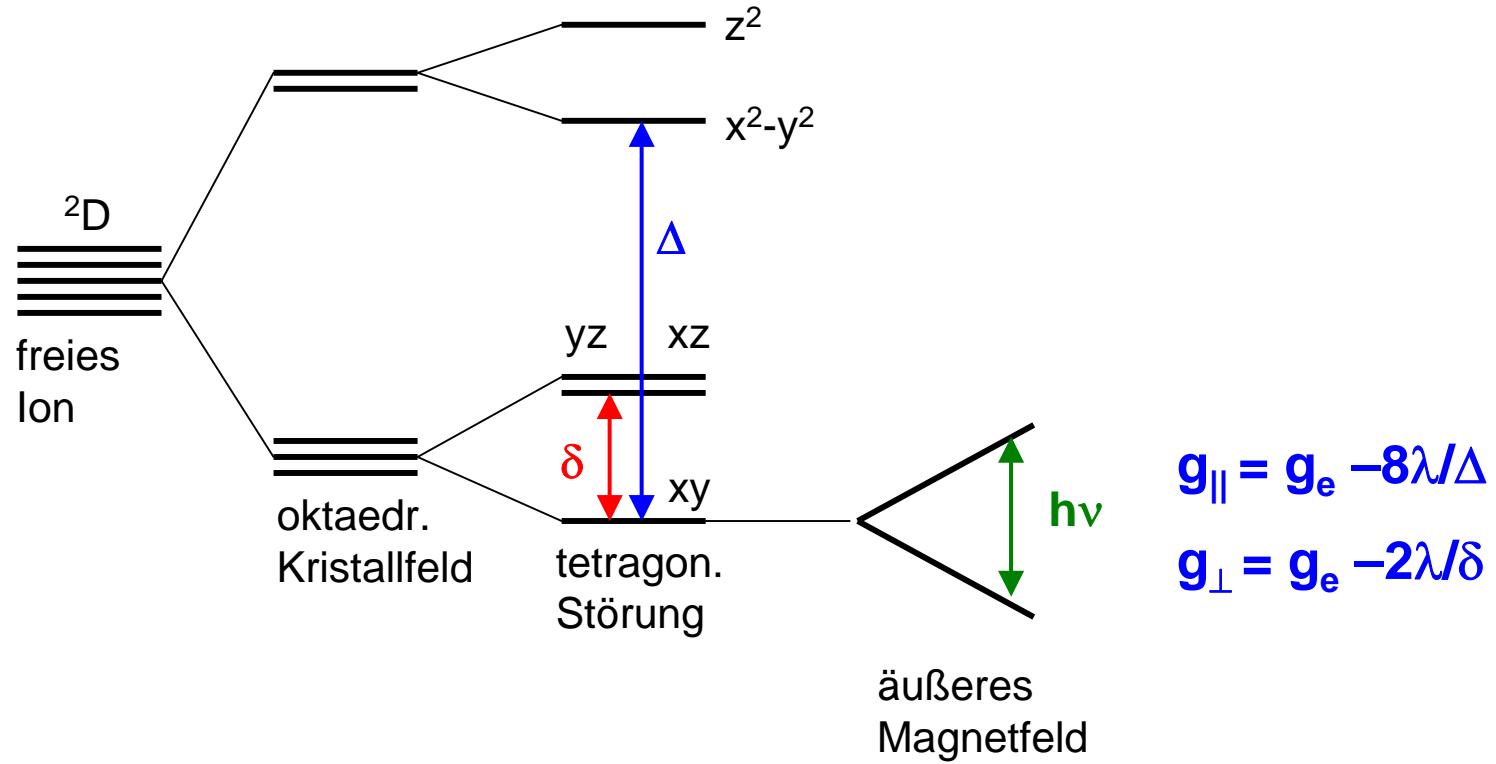


$$E_{dipolar} = -\frac{\mu_0}{4\pi} \frac{3\cos^2\theta - 1}{r^3} \mu_{nz} \mu_{ez}$$

# Pulver-ESR-Spektrum von $\text{VO}^{2+}$



# Abhangigkeit des V<sup>4+</sup>-ESR-Spektrums von der Koordinationsgeometrie (oktaedrisch, VO<sup>2+</sup>)



fur  $VOSO_4 \cdot 5 H_2O$

$$g_{||} = 1,878$$

$$g_{\perp} = 1,963$$

$$\delta = 12900 \text{ cm}^{-1}$$

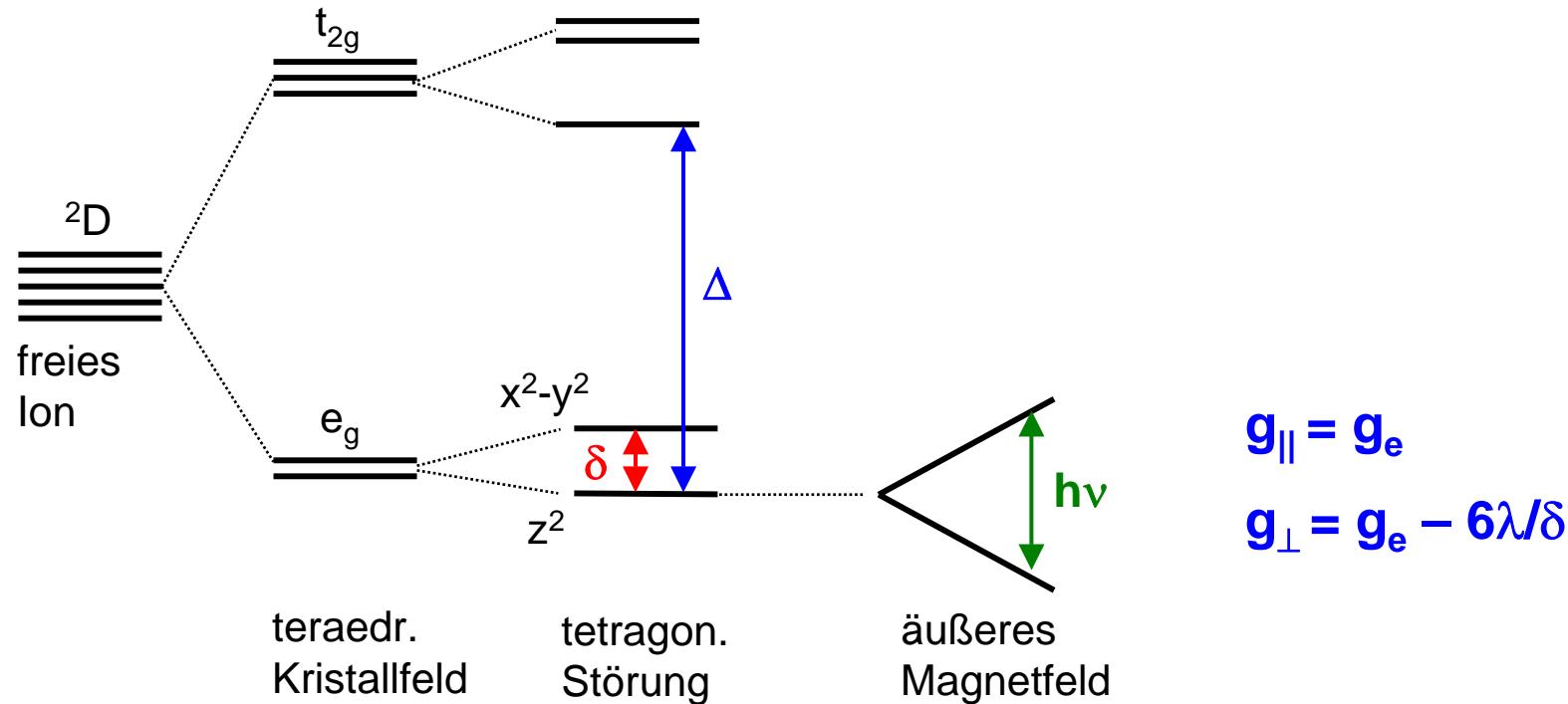
$$\Delta = 16100 \text{ cm}^{-1}$$

$$g_{||} = g_e - 8\lambda/\Delta$$

$$g_{\perp} = g_e - 2\lambda/\delta$$

$$\lambda (V^{4+}) = 250 \text{ cm}^{-1}$$

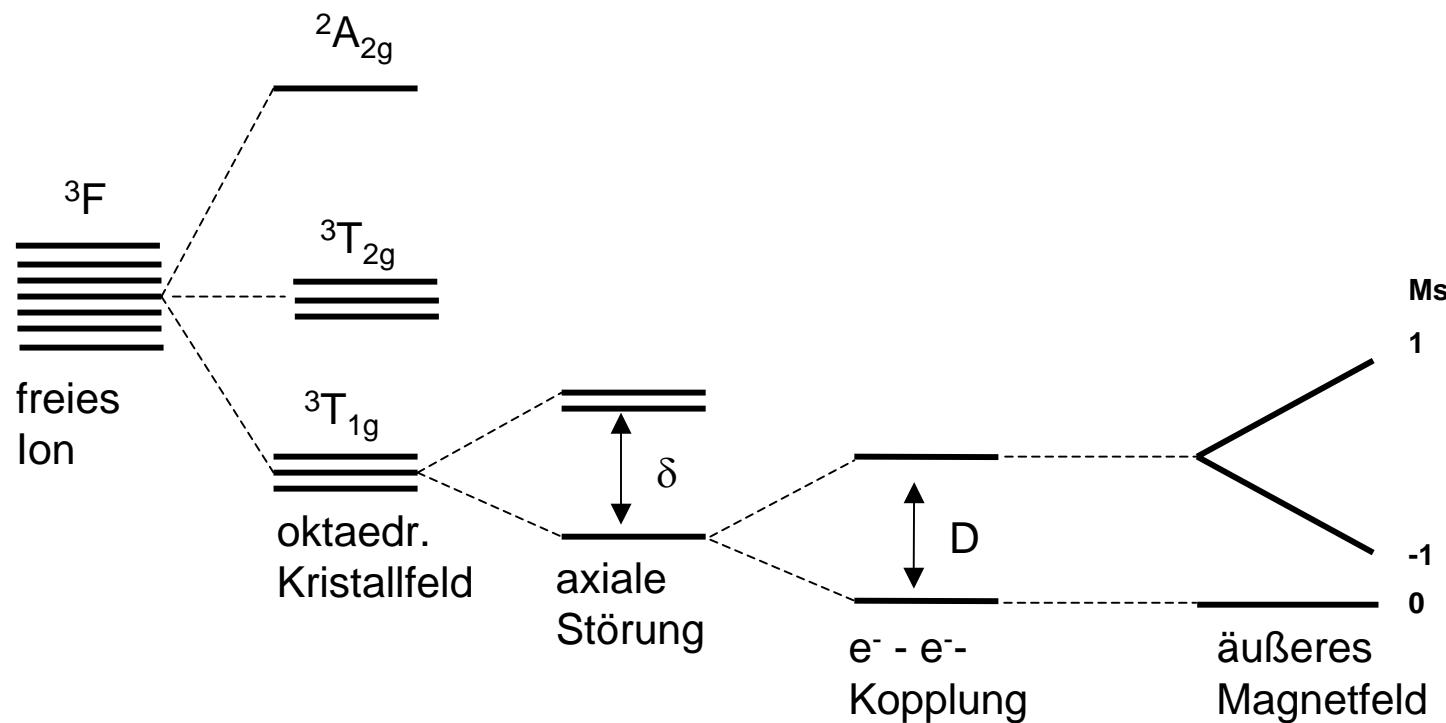
# Abhangigkeit des V<sup>4+</sup>-ESR-Spektrums von der Koordinationsgeometrie (tetraedrisch)



$\Delta E \approx h/2\pi\tau \rightarrow$  kurze Relaxationszeiten, groe Linienbreiten

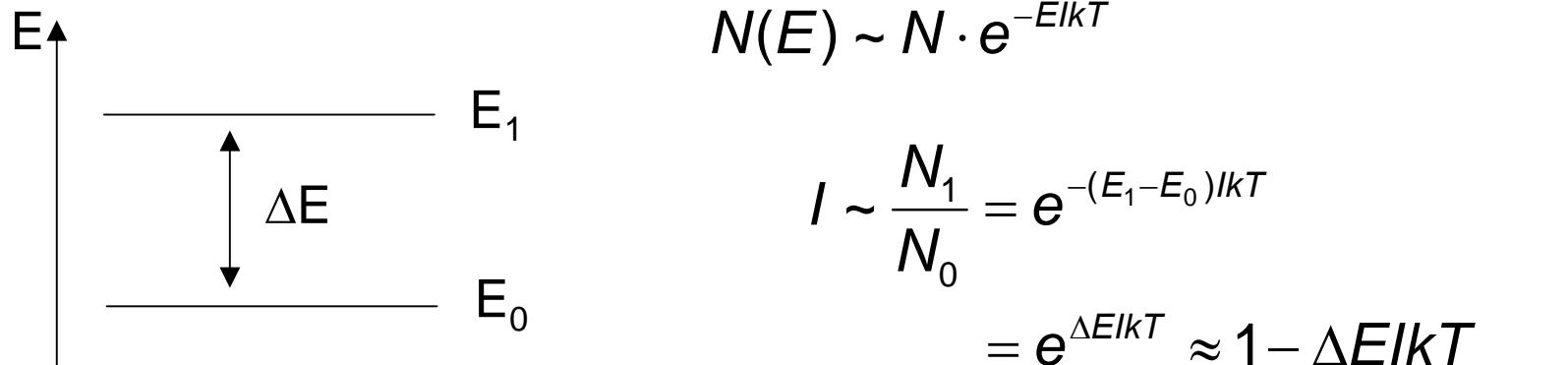
# EPR von V<sup>3+</sup> (d<sup>2</sup>)

---

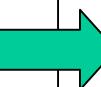


# Intensität von EPR-Signalen

---



$$I \sim \frac{N_1}{N_0} \approx 1 - \frac{g\beta B_o}{kT}$$



im X-Band ca. 0,999

vorteilhaft: Messung bei  
tiefen T und großem  $B_o$

## Temperaturabhängigkeit der Signalintensität

---

$$\vec{M} \approx N_v \vec{\mu} \quad I \sim \chi_m = \frac{M \cdot \mu_m}{B} \quad M = \frac{N_v \mu^2 B}{3kT} \text{ (therm. Gleichgewicht)}$$

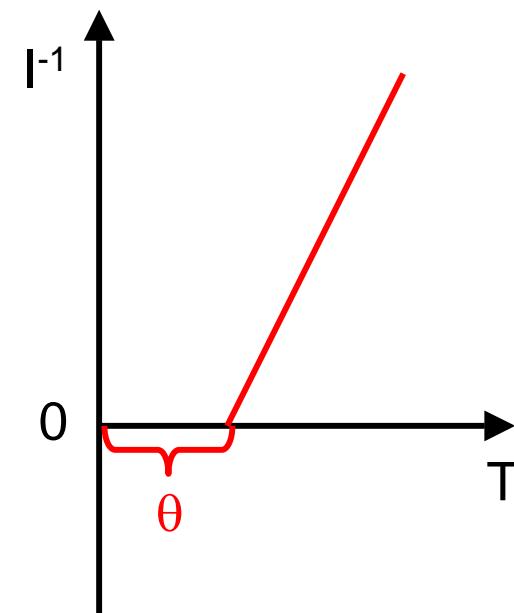
$$I \sim \chi_m = \frac{N_v g^2 \beta^2 S(S+1) \mu_m}{3k} \cdot \frac{1}{T}$$

$$\boxed{\chi_m = \frac{C}{T}}$$

Curie

$$\boxed{\chi_m = \frac{C}{T - \Theta}}$$

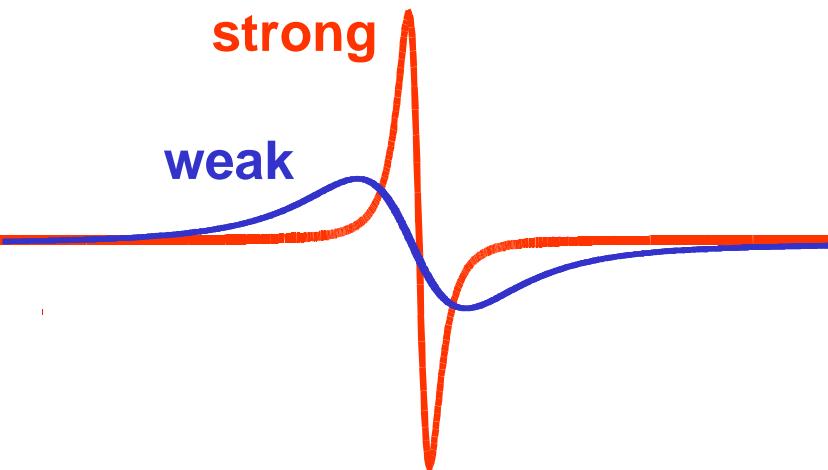
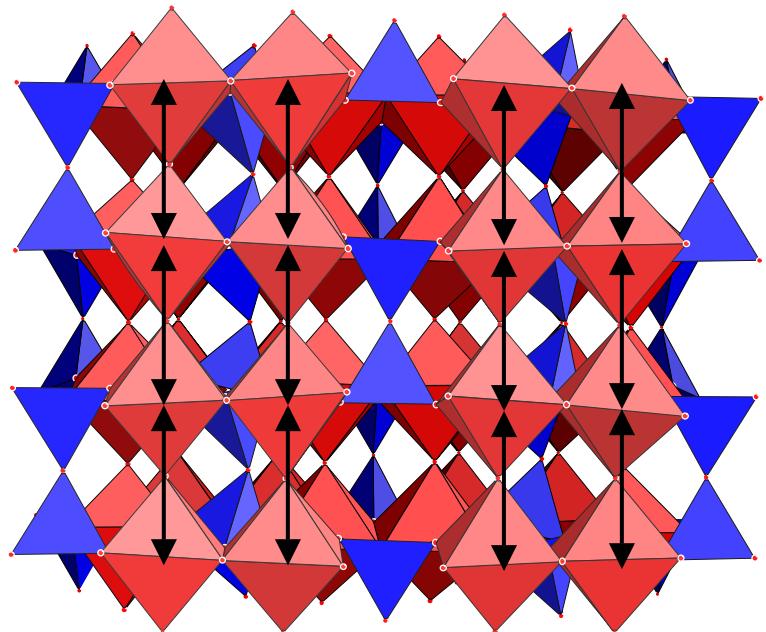
Curie - Weiß



# Magnetische Wechselwirkung von VO<sup>2+</sup> in (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>

---

Spin-spin exchange



Measure of exchange efficiency:

$\Delta E$  – exchange energy

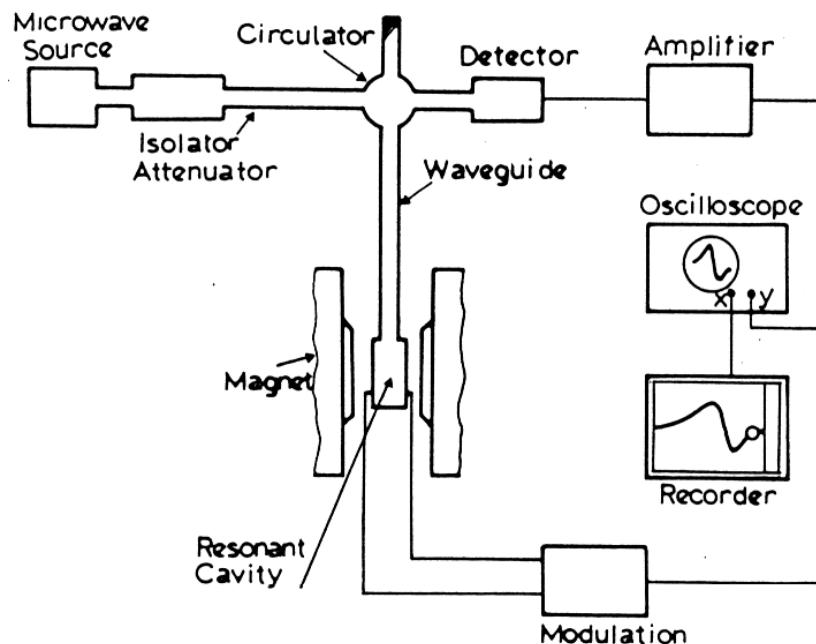
$J$  – exchange integral  
(when crystal structure is known)

$$J = \frac{\Delta E}{2zS_i(S_i + 1)}$$

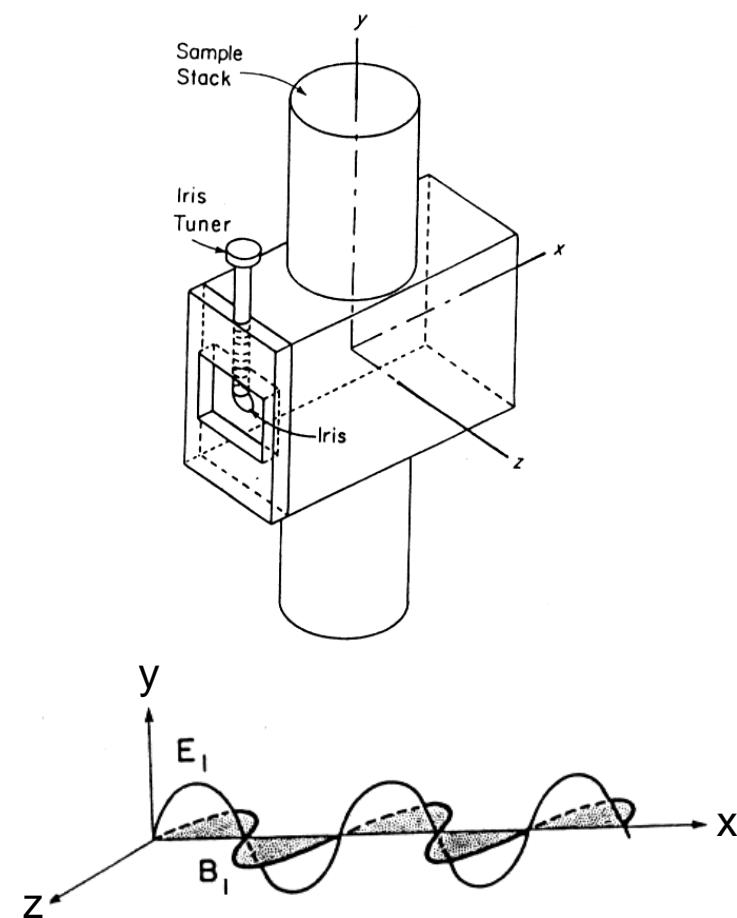
# EPR – apparatus Details

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Spektrometer-Aufbau



Rechteck-Hohlraumresonator

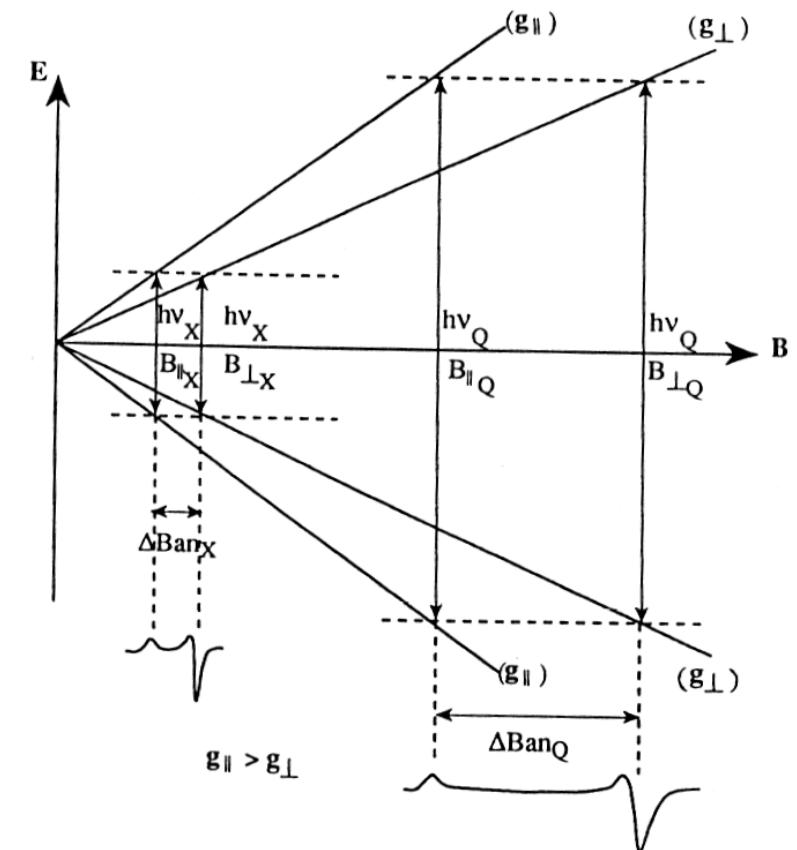


# Einfluss der Mikrowellenfrequenz

---

Band	$\nu / \text{GHz}$	$B_R / \text{mT}$	$\lambda / \text{cm}$
L	1,5	54	19,9
S	3,0	111	9,3
X	9,5	350	2,9
K	25,0	890	1,1
Q	35,0	1250	0,8
W	95,0	3400	0,3

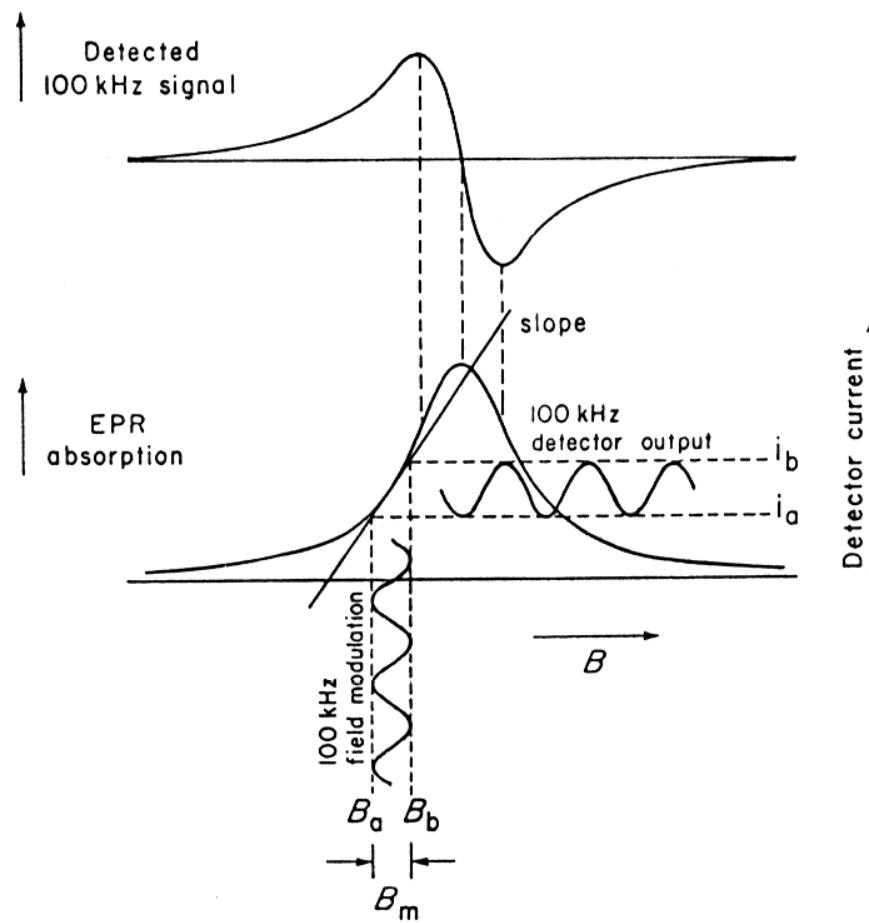
$$\Delta E = h\nu = g_e \beta B_o$$



$$H = \beta \vec{B} \cdot \hat{g} \cdot \hat{S} + \hat{S} \cdot \hat{A} \cdot \hat{I} + \hat{S} \cdot \hat{D} \cdot \hat{S}$$

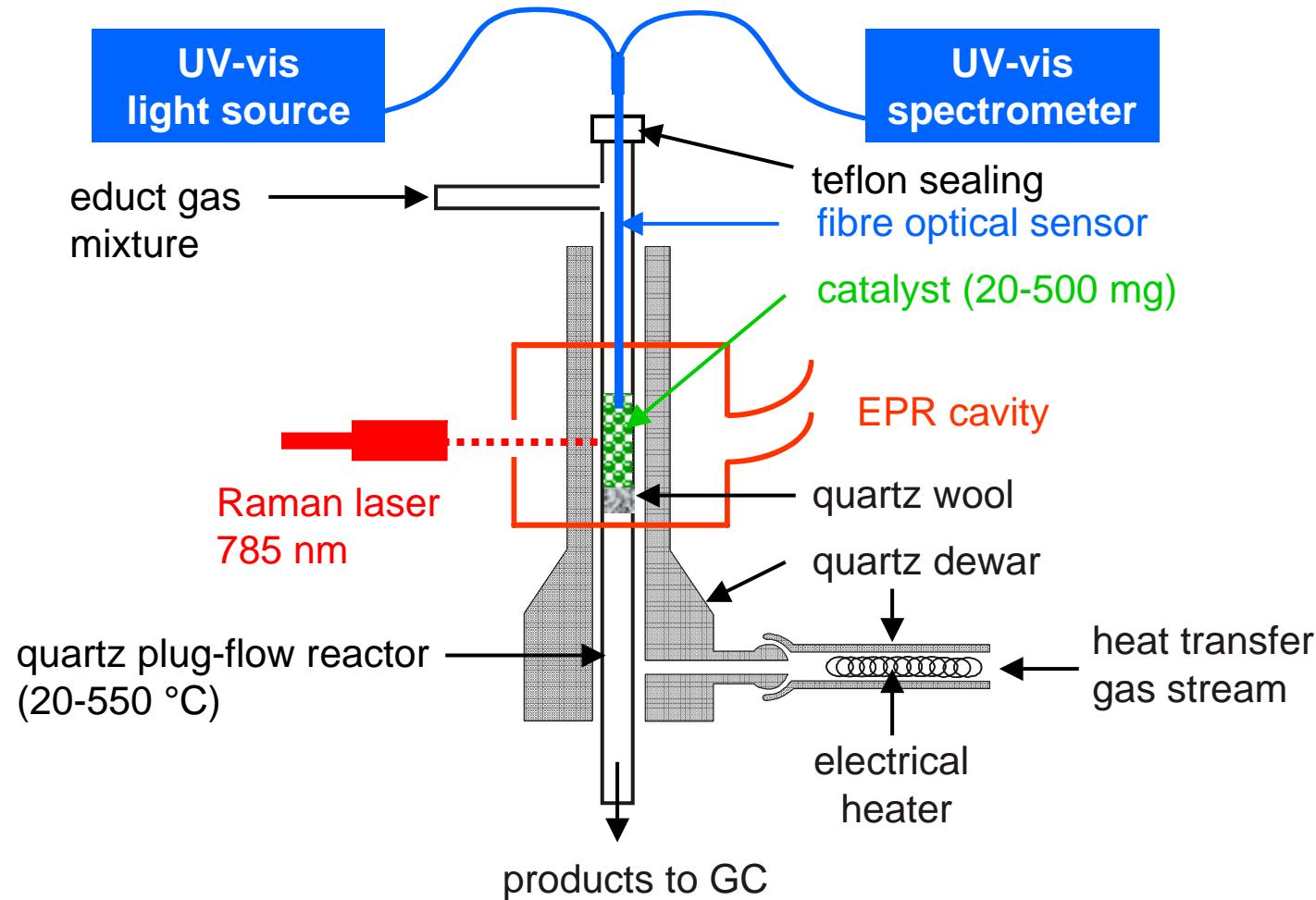
# Feld-Modulation und Signalform

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# Operando-EPR/UV-vis/Raman-Kopplung am ACA

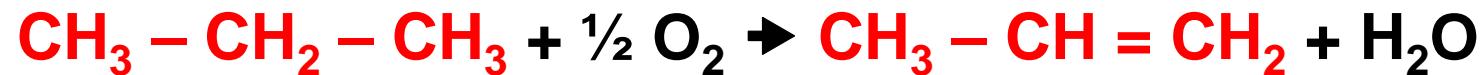
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## Anwendungsbeispiel I

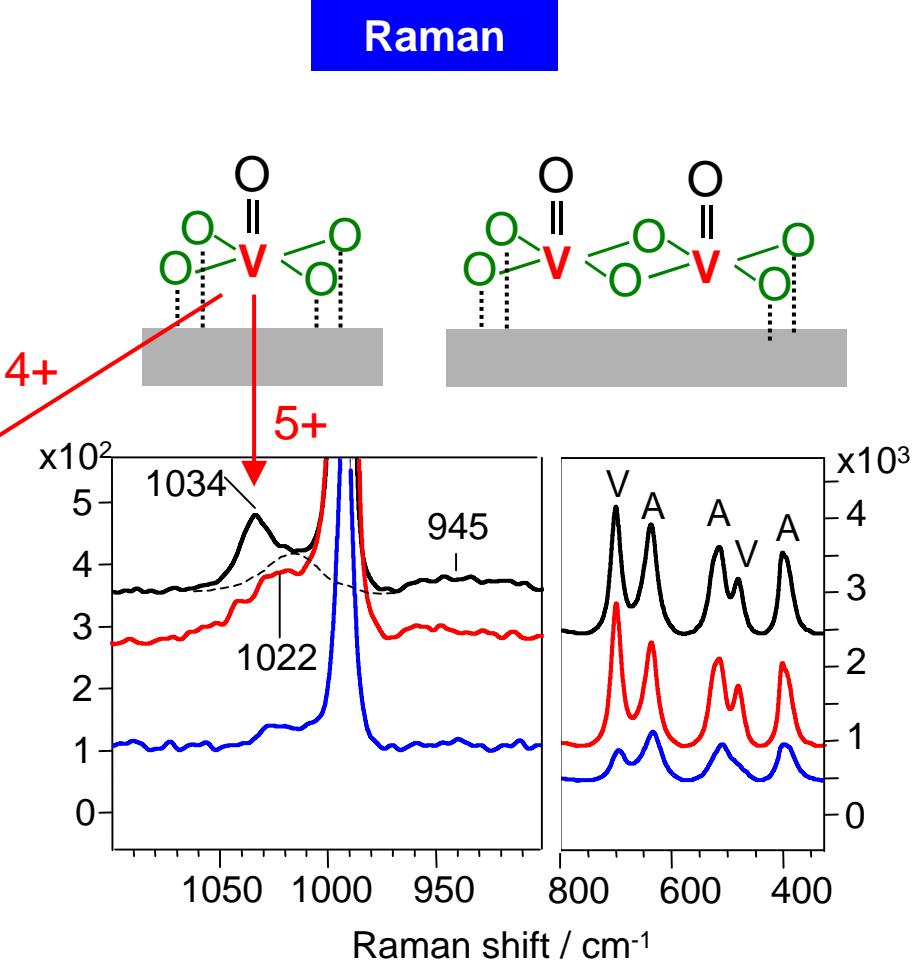
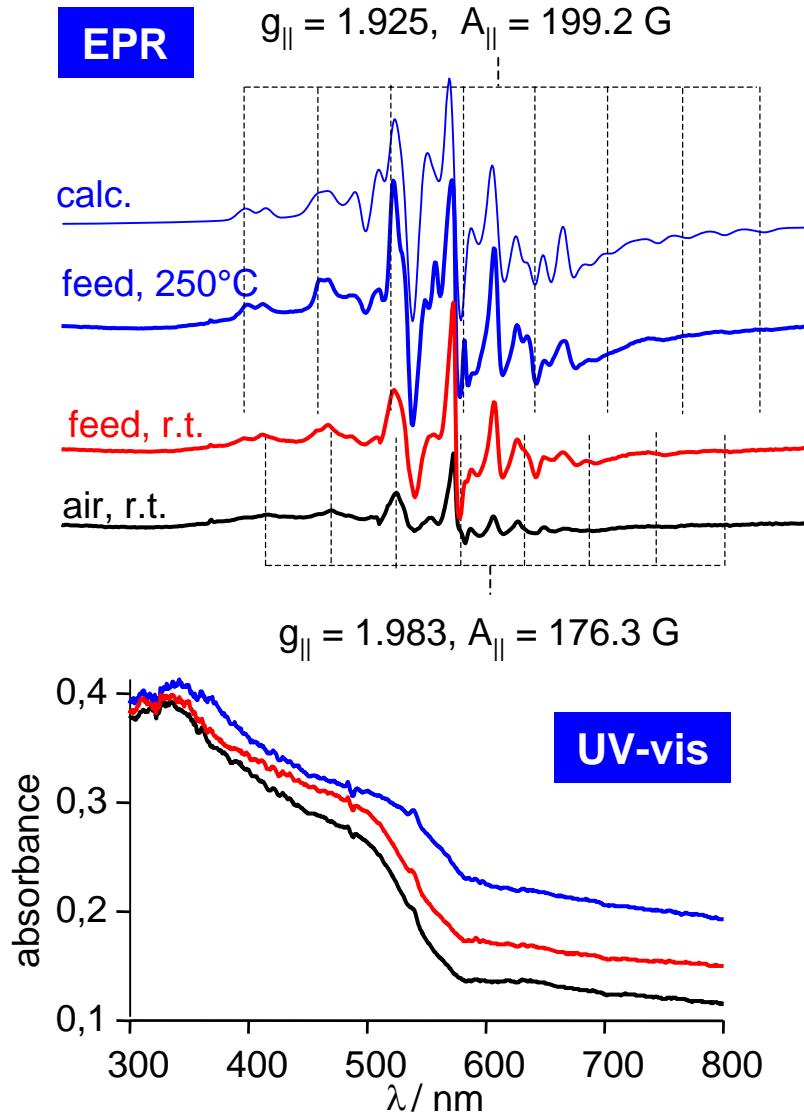
---

Oxidative Dehydrierung von Propan an  
einem 6 % V/TiO<sub>2</sub> – Trägerkatalysator



**6% V/anatase (2.2% sulfate)**  
**8.3 % C<sub>3</sub>H<sub>8</sub>, 8.3 % O<sub>2</sub> / N<sub>2</sub> up to 250°C**

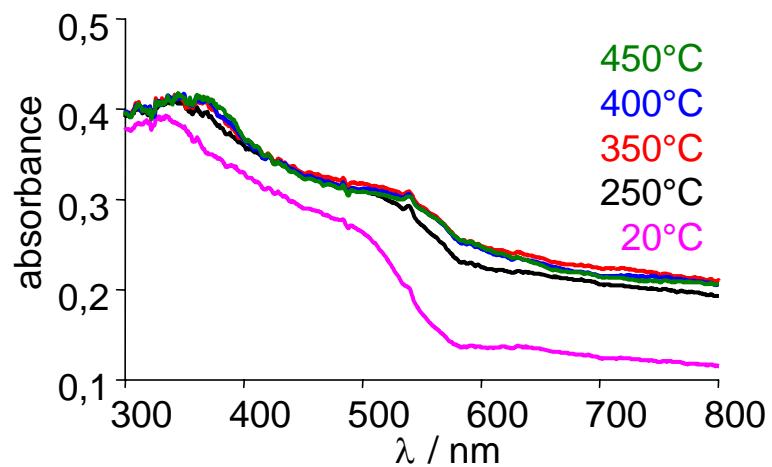
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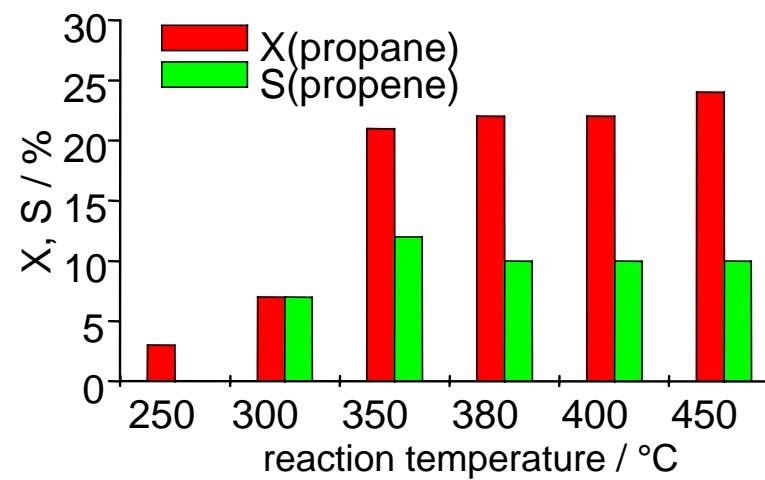
**8.3 % C<sub>3</sub>H<sub>8</sub>, 8.3 % O<sub>2</sub> / N<sub>2</sub> at 250 – 450 °C**

---

**UV-vis**



**catalysis**

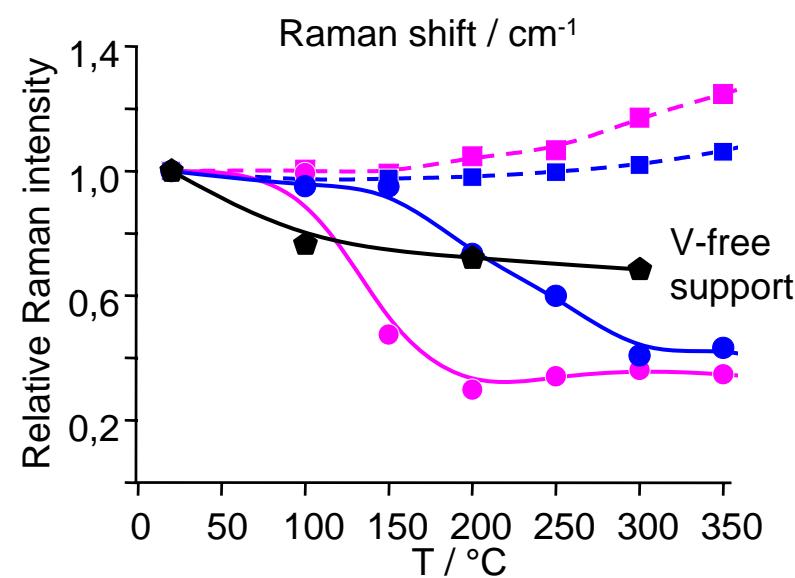
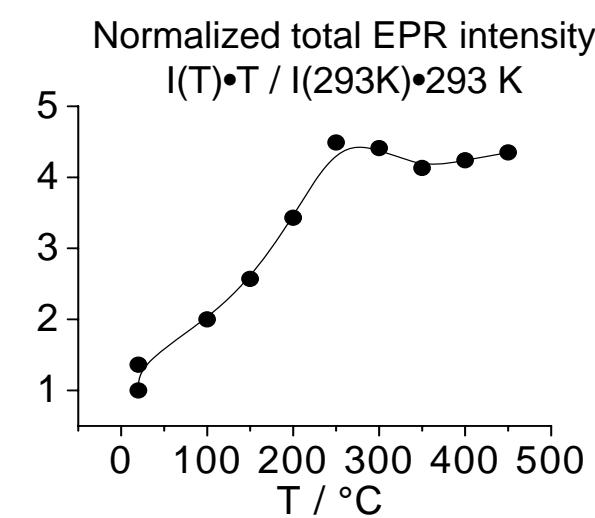
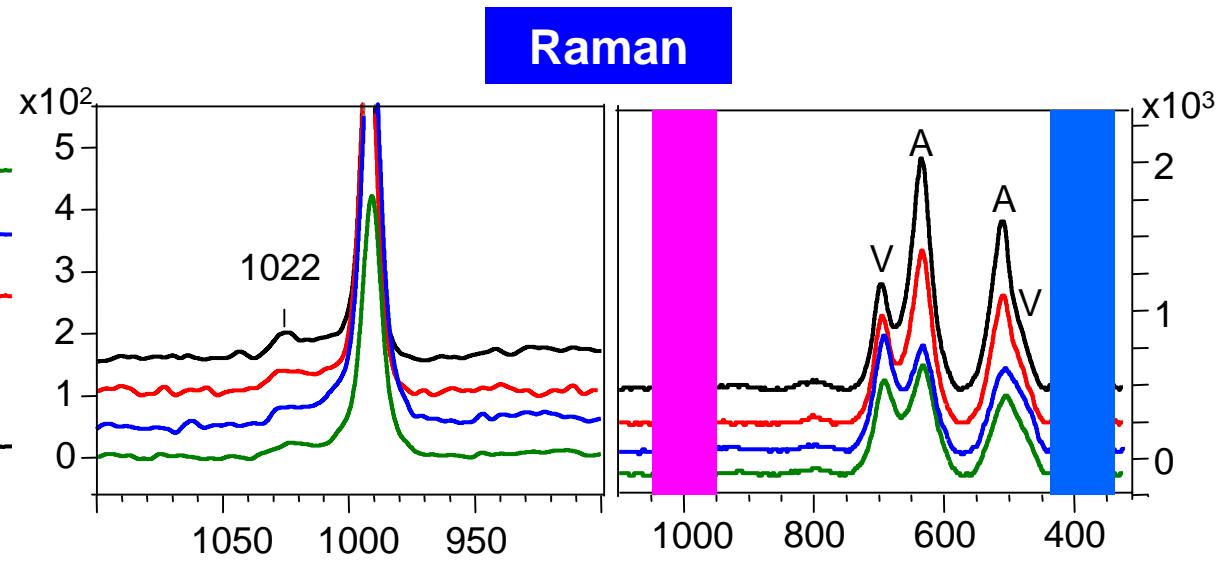
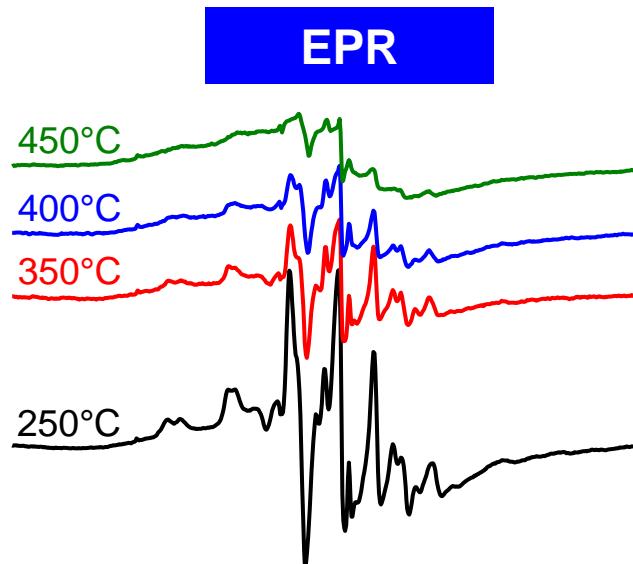


→ V reduction almost completed above 250°C

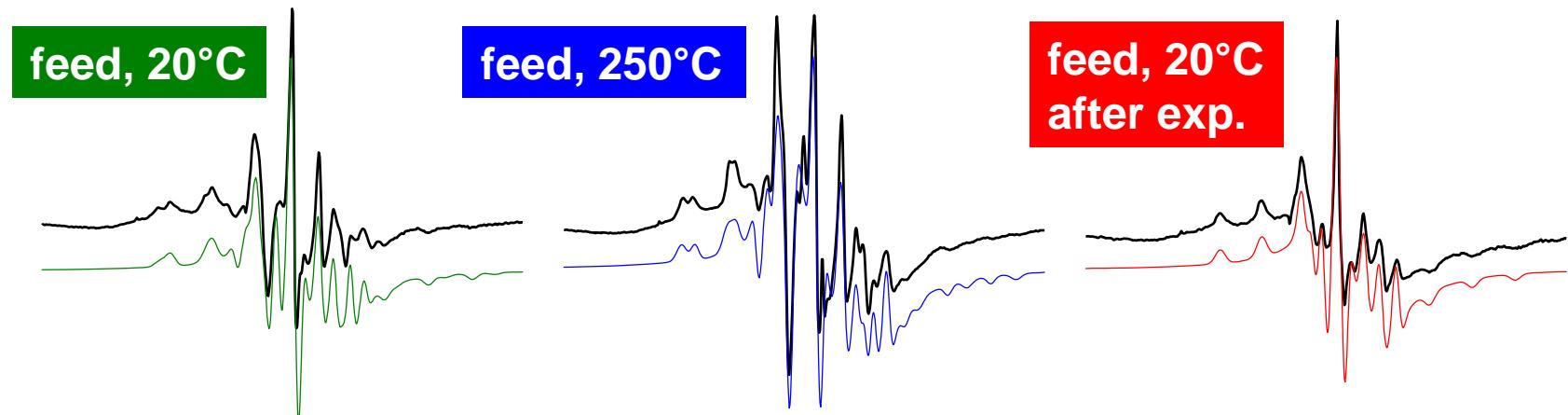
Selectivity increases with V reduction

## 8.3 % C<sub>3</sub>H<sub>8</sub>, 8.3 % O<sub>2</sub> / N<sub>2</sub> at 250 – 450 °C

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## Nature of two different isolated VO<sup>2+</sup>



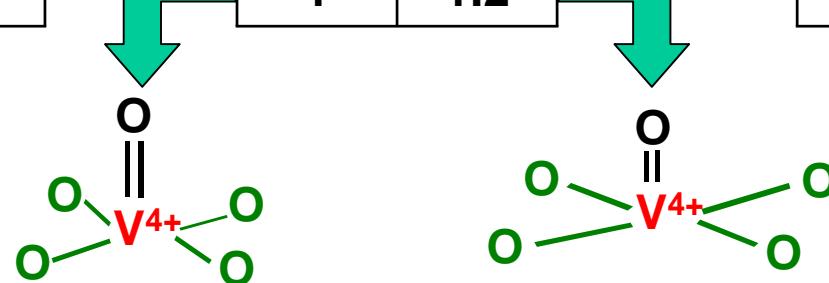
	A	B
$\Delta g_{  }/\Delta g_{\perp}$	2.16	4.00
$A_{  }/G$	180.1	199,2
$\beta_2^{*2}$	0.85	0.87
$I_{\text{rel}}$	1	0.4

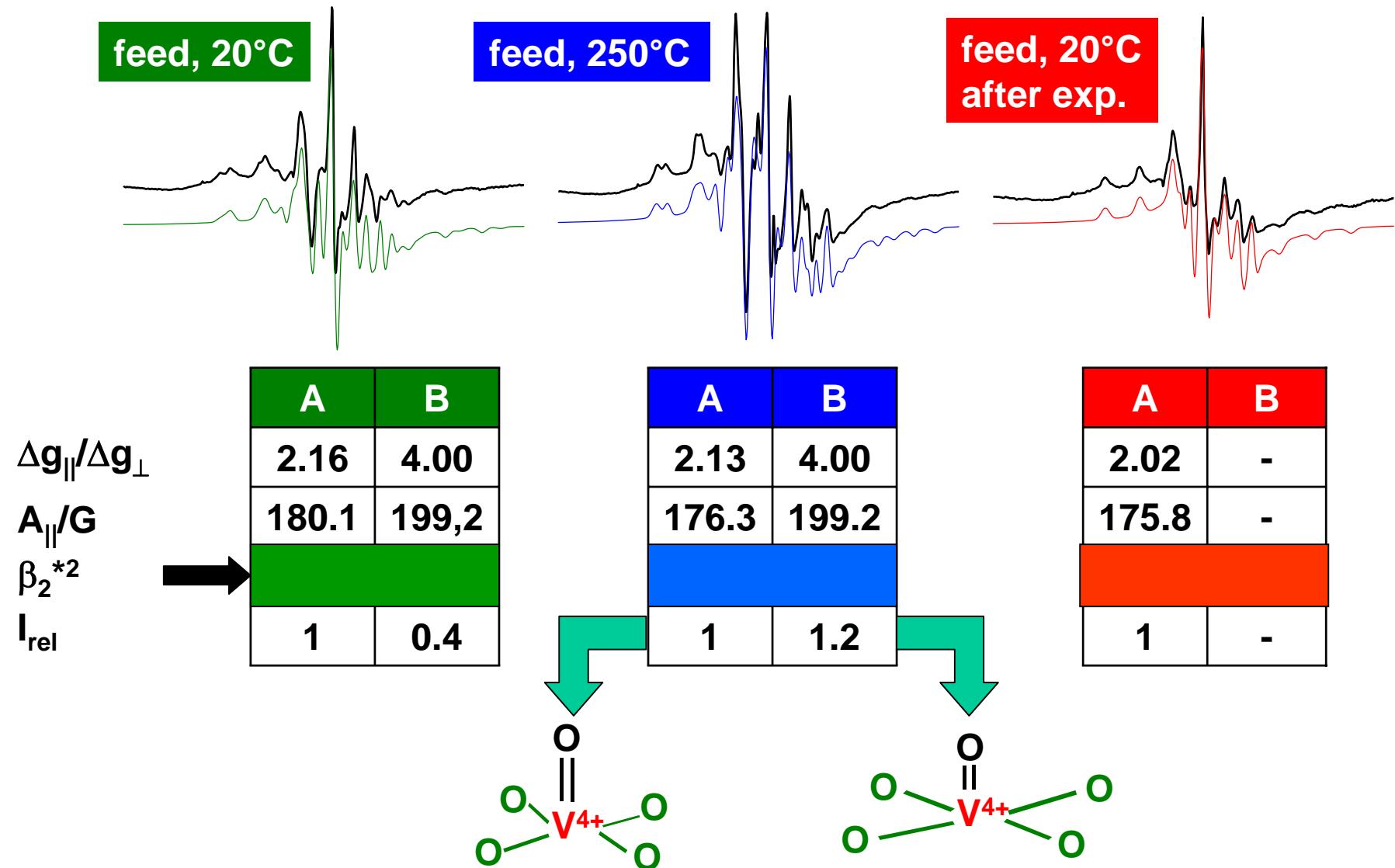
	A	B
$\Delta g_{  }/\Delta g_{\perp}$	2.13	4.00
$A_{  }/G$	176.3	199.2
$\beta_2^{*2}$	0.82	0.86
$I_{\text{rel}}$	1	1.2

	A	B
$\Delta g_{  }/\Delta g_{\perp}$	2.02	-
$A_{  }/G$	175.8	-
$\beta_2^{*2}$	0.83	-
$I_{\text{rel}}$	1	-

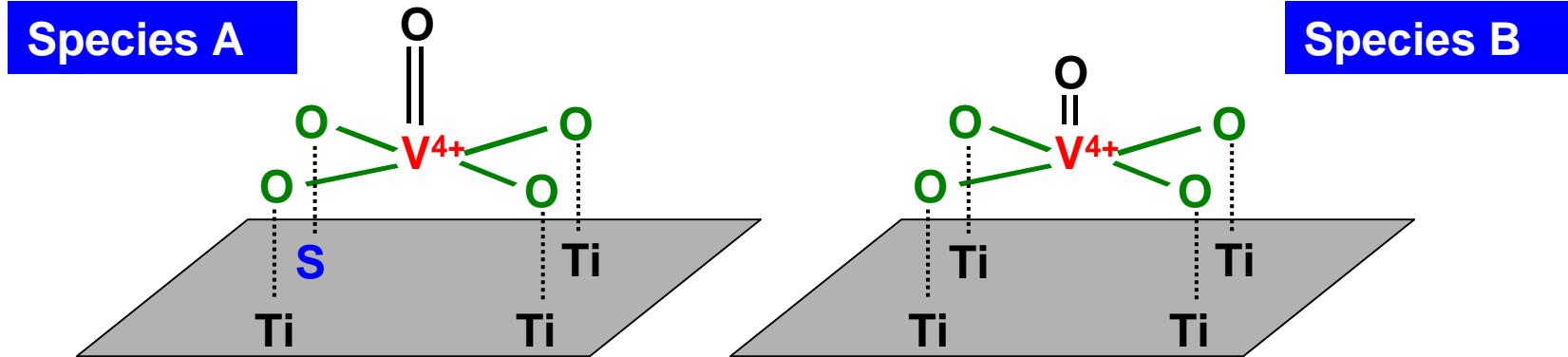


## Nature of two different isolated $\text{VO}^{2+}$



# Influence of sulfate

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- on sulfate-free anatase only species B observed  
A. Brückner et al., *Z. Anorg. Allg. Chem.* **631**, 60, 2005
- hints for bonding of  $\text{VO}^{2+}$  and/or  $\text{VO}^{3+}$  to  $\text{SO}_4$  also from FTIR and thermal analysis
- sulfate might stabilize  $\text{VO}^{2+}$  as active species on the surface
  - prevents reduction to  $\text{V}^{3+}$
  - prevents agglomeration
  - prevents diffusion into the bulk of the support

## Literatur

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